Chemical Science

Paper III

Time Allowed : 2½ Hours] **[Maximum Marks : 150**

Note : This Paper contains **Seventy Five (75)** multiple choice questions, each question carrying **Two (2)** marks. Attempt *All* questions.

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1. An electron of mass '*m*' is confined to a 1-D box of length 'L'. It makes a radiative transition from second excited state to ground state. The wavenumber of the photon emitted is :

(A) $\frac{h}{mL^2c}$ (B) $\frac{2h}{mL^2c}$

(C) $\frac{9h}{mL^2c}$ (D) $\frac{3h}{mL^2c}$

2. The wave function of a 1-D harmonic oscillator between $x = -\infty$ and $x = +\infty$ is given by :

$$\psi(x) = N \exp\left(-\frac{\beta x^2}{2}\right).$$

$$\left(\text{Given : } \int_0^\infty e^{-ax^2}dx = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}\right)$$

The value of N, that normalizes the function $\psi(x)$, is :

(A) $\left(\frac{\beta}{\pi}\right)^{1/2}$ (B) $\left(\frac{\beta}{\pi}\right)^{1/4}$

(C) $\left(\frac{\beta}{2\pi}\right)^{1/2}$ (D) $\left(\frac{\pi}{\beta}\right)^{1/4}$

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3. The molecular orbitals of 1, 3-butadiene (*not in proper order*) are given below :

(f_1, f_2, f_3, f_4 are the $2p_z$ orbitals on carbon atoms 1, 2, 3 and 4 respectively).

$\psi_1 = 0.372f_1 - 0.602f_2 + 0.602f_3 - 0.372f_4$.

$\psi_2 = 0.602f_1 + 0.372f_2 - 0.372f_3 - 0.602f_4$.

$\psi_3 = 0.372f_1 + 0.602f_2 + 0.602f_3 + 0.372f_4$.

$\psi_4 = 0.602f_1 - 0.372f_2 - 0.372f_3 + 0.602f_4$.

The HOMO and LUMO in the ground state of 1, 3-butadiene are respectively :

(A) ψ_2 and ψ_3 (B) ψ_3 and ψ_2

(C) ψ_2 and ψ_4 (D) ψ_2 and ψ_1

4. The $J = 0 \rightarrow 1$ rotational transition for $H^{79}Br$ occurs at 500.72 GHz. Assuming the molecule to be a rigid rotor, the $J = 4 \rightarrow 5$ transition occurs at :

(A) 50.1 cm^{-1} (B) 66.8 cm^{-1}

(C) 16.7 cm^{-1} (D) 83.5 cm^{-1}

5. The following data are obtained for the vibration-rotation spectrum of a diatomic molecule :

J	$\bar{\nu}[R(J)]/cm^{-1}$	$\bar{\nu}[P(J)]/cm^{-1}$
0	2642.60	—
1	2658.36	2609.67
2	—	2592.51

The value of the rotational constant $\bar{B}_0$ in the ground vibrational state is :

(A) 8.12 cm^{-1} (B) 8.35 cm^{-1}

(C) 8.58 cm^{-1} (D) 7.88 cm^{-1}

6. Assuming H_2 and HD molecules having equal bond lengths, the ratio of rotational partition functions of these molecules using high temperature approximation is :

(A) 3/8 (B) 3/4

(C) 1/2 (D) 2/3

7. Which of the following statements is *not* true for entropy production in a system ?

(A) Rate of entropy production in a system is a product of flux and driving force.

(B) Rate of entropy production is always positive for a spontaneous process.

(C) Rate of entropy production is always negative for a spontaneous process.

(D) Rate of entropy production is zero at equilibrium.

8. The Slater determinant (un-normalized) for the ground state of lithium atom is :

(A) $\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$

(B) $\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 1s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 1s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 1s(3)\alpha(3) \end{vmatrix}$

(C) $\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 1s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 1s(3)\beta(3) \end{vmatrix}$

(D) $\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) & 2s(2)\beta(2) \\ 1s(3)\alpha(3) & 2s(3)\alpha(3) & 2s(3)\beta(3) \end{vmatrix}$

9. If the $t_{1/2}$ of a radioactive element is 10 d, the number of days required to reduce it to 1/8th of its original value is :

(A) 10 d (B) 20 d

(C) 30 d (D) 80 d

10. In the reaction $N_2O_4(g) \leftrightarrow 2NO_2(g)$ an increase in pressure would result in :

(A) Increase in the amount of product

(B) Increase in the amount of reactant

(C) Have no effect on equilibrium

(D) Initial increase and then decrease in the amount of product formed.

11. The pressure just below the meniscus of water is :

(A) Greater than just above it.

(B) Less than just above it.

(C) Same as just above it.

(D) Always equal to atmospheric pressure.

12. Bakelite is obtained by reaction between :

(A) Phenol and formaldehyde (B) Benzene and formaldehyde

(C) Benzophenol and acetic acid (D) Phenol and acetic acid

13. The boiling temperature of ethyl benzene is 136°C. Use Trouton's rule to determine the enthalpy of vaporization of ethyl benzene at this temperature :

(A) 35 kJ mol^{-1} (B) 12 kJ mol^{-1}

(C) 23 kJ mol^{-1} (D) 4.8 kJ mol^{-1}

14. The isotope used for diagnosing hyperthyroiditis is :

(A) ^{125}I (B) ^{127}I

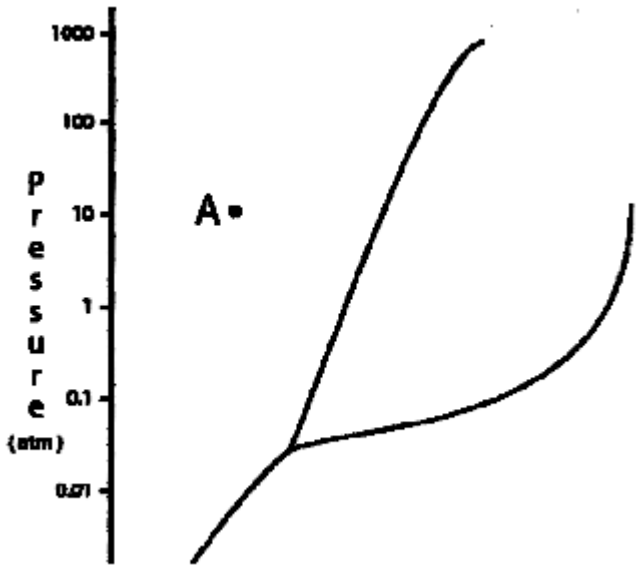
(C) ^{130}I (D) ^{128}I

15. Reaction quotient for the reaction, $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$ is given as :

(A) $Q = \frac{p_{NO}^4 \cdot p_{H_2O}^6}{p_{NH_3}^4 \cdot p_{O_2}^5}$ (B) $Q = \frac{[NO]^4 [H_2O]^6}{[NH_3]^4 \cdot [O_2]^5}$

(C) $Q = \frac{a_{NO}^4 \cdot a_{H_2O}^6}{a_{NH_3}^4 \cdot a_{O_2}^5}$ (D) $Q = \frac{m_{NO}^4 \cdot m_{H_2O}^6}{m_{NH_3}^4 \cdot m_{O_2}^5}$

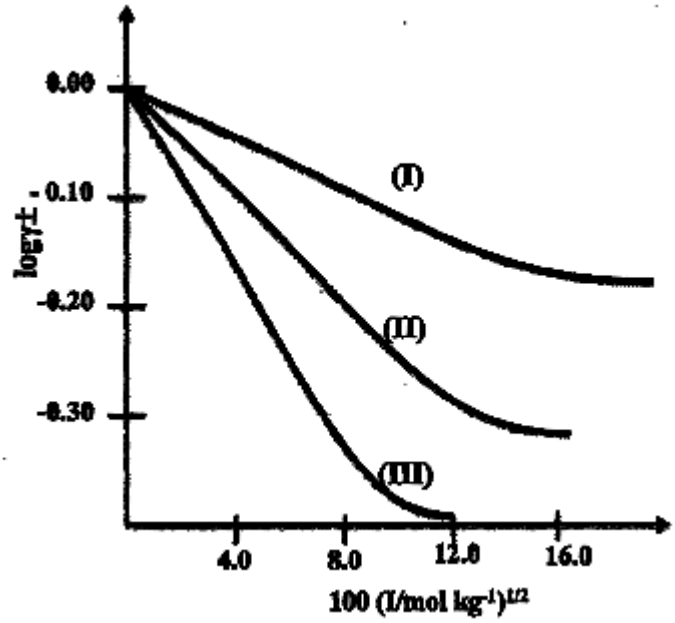
16. In the following phase diagram, phase of a substance marked as point A will be :



(A) Solid (B) Liquid

(C) Gas (D) Supercritical fluid

17. Plots of log $\gamma \pm$ *vs.* $\sqrt{c}$ for the electrolytes; $MgSO_4$, NaCl and $MgCl_2$ are given below. Base on that the plots marked as (I), (II) and (III) belong to :



(A) I ≡ $MgSO_4$, II ≡ NaCl and III ≡ $MgCl_2$

(B) I ≡ NaCl, II ≡ $MgCl_2$ and III ≡ $MgSO_4$

(C) I ≡ $MgCl_2$, II ≡ NaCl and III ≡ $MgSO_4$

(D) I ≡ $MgSO_4$, II ≡ $MgCl_2$ and III ≡ NaCl

18. The galvanic cell, $Cr|Cr^{2+}(aq.)||Ag^{+}(aq.)|Ag$ is short-circuited and current is allowed to pass through it spontaneously. The changes in concentrations of Cr^{2+} and Ag^{+}, and masses of electrodes will be in the following order :

	$[Cr^{2+}]$	**$[Ag^{1+}]$**	**Mass of Ag electrode**	**Mass of Cr electrode**
(A)	decrease	decrease	increase	increase
(B)	decrease	increase	decrease	increase
(C)	increase	decrease	increase	decrease
(D)	increase	increase	decrease	decrease

19. For the oscillating reaction having Lotka-Volterra mechanism,

$$A + X \xrightarrow{k_1} 2X$$

$$X + Y \xrightarrow{k_2} 2Y$$

$$Y \xrightarrow{k_3} Z$$

The concentration of the reactant 'A' will :

(A) Oscillate with time.

(B) Increase exponentially with time and remain constant.

(C) Remain constant throughout the reaction.

(D) Decrease exponentially with time and will become zero.

20. Consider the equilibrium reaction,

$$H^+(aq.) + OH^-(aq.) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O(l)$$

The rate constants k_1 and k_{-1} are estimated by :

(A) Laser flash photolysis (B) Fast acid-base titration

(C) Temperature jump method (D) Time resolved pH metry

21. For the reaction X + Y + Z $\rightarrow$ P, the experimental data for the measured initial rates are given below :

Run	$[X]_0$, (M)	$[Y]_0$, (M)	$[Z]_0$, (M)	**Initial Rates** $R_0\left(Ms^{-1}\right)$
1	0.2	0.5	0.4	8.0×10^{-5}
2	0.4	0.5	0.4	3.2×10^{-4}
3	0.4	2.0	0.4	1.28×10^{-3}
4	0.2	0.5	1.6	3.2×10^{-4}

Orders of the reaction w.r. to X, Y and Z are :

(A) 2, 2, 1 (B) 2, 1, 2

(C) 2, 1, 1 (D) 1, 1, 2

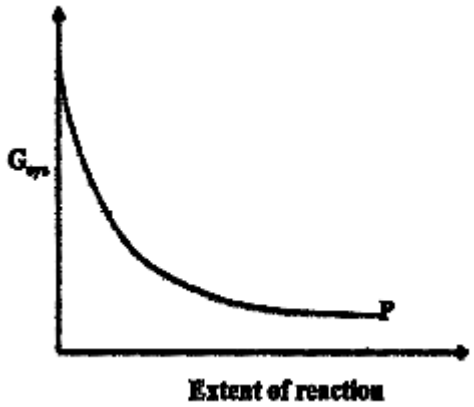
22. According to the transition state theory for the elementary bi-molecular reactions, the molar entropy of activation $\Delta S_0^{\neq}$ is :

(A) negative
(B) positive
(C) zero
(D) positive for endothermic and negative for exothermic reactions

23. For the chemical equilibrium,

$$A \rightleftharpoons B$$

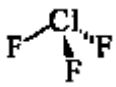
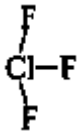
The plot of Gibbs free energy of the system (G_{sys}) *vs.* extent of reaction is shown below :



Point P, marked in the plot, corresponds to :

(A) $\mu_A > \mu_B$ (B) $\mu_B > \mu_A$
(C) $\mu_A = \mu_B$ (D) $\mu_A = \mu_B = 0$

24. The ^{19}F NMR spectrum of ClF_3 exhibits a 1 : 1 doublet and a 1 : 2 : 1 triplet. The structure of ClF_3 will be :
(Natural abundance of ^{19}F is 100%, ignore coupling with Cl nucleus.)

(A) 
(B) 
(C) 
(D) $(ClF_2)^+ F^-$

25. The Mössbauer spectrum of a foil of iron enriched with ^{57}Fe exhibits a single signal at zero velocity, when the spectrum is recorded in an applied magnetic field, it changes to a .... spectrum.

(Given : I values of ^{57}Fe is 1/2 and 3/2 in the ground and excited states respectively.)

(A) Two lines (B) Three lines

(C) Four lines (D) Six lines

26. The formation of Schottky defects should result in :

(A) The contraction of crystal lattice

(B) Decrease in the density of the crystal

(C) Decrease in electrical conductivity

(D) Increase in volume

27. The addition of gallium impurity to silicon results in :

(A) Decrease in the band gap

(B) Increase in the band gap

(C) Addition of a new intermediate band with electrons

(D) Addition of a new intermediate band with holes

28. Which statement most *correctly* describes crystal field theory for a *d*-block complex of unspecified geometry ?

(A) The theory considers covalent interaction between a metal centre and the surrounding ligands.

(B) The theory considers electrostatic interaction between a metal ion and the surrounding ligand which are taken to be point charges.

(C) The theory rationalizes the non-degeneracy of the metal-orbitals by considering the electrostatic repulsions between point charge ligands and electrons in the metal *d*-orbitals.

(D) The theory rationalizes the metal *d*-orbitals are split into two levels.

29. For which pair of the complexes is the order of values of Δ_{oct} correct ?

(A) $\left[Rh(NH_3)_6\right]^{3+} > \left[Co(NH_3)_6\right]^{3+}$

(B) $\left[Fe(CN)_6\right]^{4-} > \left[Fe(CN)_6\right]^{3-}$

(C) $\left[Cr(H_2O)_6\right]^{2+} > \left[Cr(H_2O)_6\right]^{3+}$

(D) $\left[CrF_6\right]^{3-} > \left[Cr(CN)_6\right]^{3-}$

30. $\left[Cr(CN)_6\right]^{3-}$ is expected to be :

(A) Diamagnetic
(B) Paramagnetic with $\mu_{eff} < 3.87$ BM
(C) Paramagnetic with $\mu_{eff} > 3.87$ BM
(D) Paramagnetic with $\mu_{eff} \approx 3.87$ BM

31. The reaction of $\left[PtCl_4\right]^{2-}$ with $\left[NO_2\right]^{-}$ followed by NH_3 gives :

(A) trans-$\left[PtCl(NH_3)(NO_2)_2\right]^{-}$ (B) trans-$\left[PtCl_2(NH_3)(NO_2)\right]^{-}$

(C) cis-$\left[PtCl(NH_3)_2(NO_2)\right]^{2-}$ (D) cis-$\left[PtCl_2(NH_3)(NO_2)\right]^{-}$

32. Which of the following complexes has the maximum number of unpaired electrons ?

(A) $\left[FeCl_4\right]^{-}$ (B) $\left[VO(H_2O)_5\right]^{2+}$

(C) $Hg\left[Co(NCS)_4\right]$ (D) $\left[Co(NH_3)_6\right]^{3+}$

33. The bright yellow colour of $\left[Cu(phen)_2\right]^{+}$ (phen = 1, 10-phenanthroline) is due to :

(A) *d-d* transitions
(B) intraligand charge transfer transition
(C) LMCT transition
(D) MLCT transition

34. The rate of oxygen atom transfer from various oxyhalides follows the order :

(A) $ClO_4^- < ClO_3^- < ClO^-$ (B) $IO_4^- < BrO_4^- < ClO_4^-$

(C) $ClO^- < ClO_3^- < ClO_4^-$ (D) $ClO^- < ClO_4^- < BrO_4^-$

35. Identify the following boranes with their class of boranes :

(*a*) closo (*i*) B_6H_{12}

(*b*) nido (*ii*) $(B_6H_6)^{2-}$

(*c*) arachno (*iii*) B_6H_{10}

(A) (*a*)—(*iii*), (*b*)—(*i*), (*c*)—(*ii*)

(B) (*a*)—(*i*), (*b*)—(*iii*), (*c*)—(*ii*)

(C) (*a*)—(*ii*), (*b*)—(*i*), (*c*)—(*iii*)

(D) (*a*)—(*ii*), (*b*)—(*iii*), (*c*)—(*i*)

36. The structure of $[IF_6]^-$ is best described as :

(A) trigonally distorted octahedron

(B) octahedron

(C) square pyramid

(D) trigonal bipyramid

37. Among the following statements :

(*a*) Orthosilicates have general formula $(SiO_4)^{4-}$

(*b*) $BaTiSi_3O_9$ is an example for cyclosilicate

(*c*) $Si_2O_7^{6-}$ is an orthosilicate

(*d*) $ZrSiO_4$ is a pyrosilicate

(A) (*a*), (*b*) are correct (B) (*a*), (*c*) are correct

(C) only (*a*) is correct (D) (*c*), (*d*) are correct

38. The type of hybridisation of carbon in carbon nanotube is :

(A) sp and sp^2 (B) sp^2 and sp^3

(C) sp and sp^3 (D) sp, sp^2 and sp^3

39. Which one of the following pairs consists of the naturally occurring actinides ?

(A) Am, Cf (B) Th, Po

(C) Th, U (D) U, Am

40. In the ion exchange separation of lanthanides :

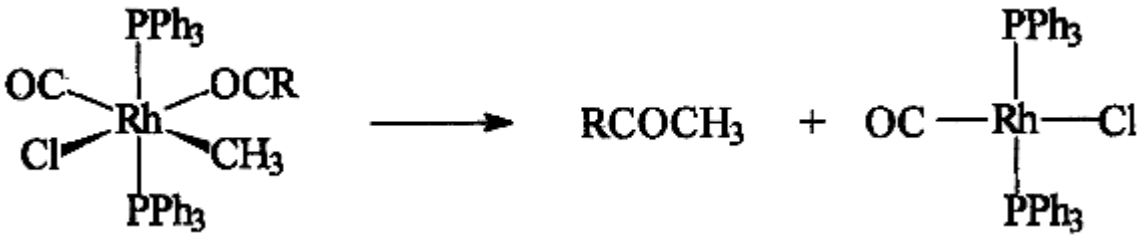
(A) La(III) gets eluted first because of its larger size

(B) La(III) gets eluted first because of the smaller size of its hydrated ions

(C) Lu(III) gets eluted first because of the larger size of its hydrated ions

(D) Lu(III) gets eluted first because of its smaller size

41. Identify the type of the reaction given below :



(A) Oxidative addition (B) Oxidative elimination

(C) Carboxylation (D) Reductive elimination

42. Which of the following can act as an oxidising agent ?

(A) $\left[Mo\left(\eta^5\text{-}C_5H_5\right)_2\right]$ (B) $\left[Fe\left(\eta^5\text{-}C_5H_5\right)_2\right]$

(C) $\left[Co\left(\eta^5\text{-}C_5H_5\right)_2\right]$ (D) $\left[Ru\left(\eta^5\text{-}C_5H_5\right)_2\right]$

43. The *correct* order of the strength of M-C bond in the given carboxyls is :

(A) $\left[V(CO)_6\right]^- > \left[Cr(CO)_6\right] > \left[Mn(CO)_6\right]^+$

(B) $\left[Cr(CO)_6\right] < \left[Mn(CO)_6\right]^+ < \left[V(CO)_6\right]^-$

(C) $\left[Cr(CO)_6\right] > \left[Mn(CO)_6\right]^+ > \left[V(CO)_6\right]^-$

(D) $\left[V(CO)_6\right]^- < \left[Cr(CO)_6\right] < \left[Mn(CO)_6\right]^+$

44. In deoxymyoglobin the iron centre is best described as :

(A) low-spin Fe(III) (B) low-spin Fe(II)

(C) high-spin Fe(II) (D) high-spin Fe(III)

45. Which of the following copper biomolecules is EPR silent ?

(A) superoxide dismutase (B) oxyhemocyanin

(C) plastocyanin (D) nitrite reductase

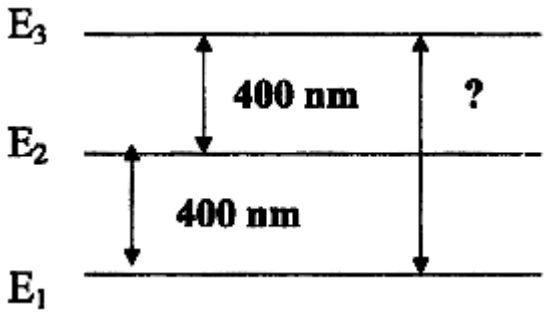
46. The active site structure of Rieske protein can be best described as :

(cys = cysteine and his = histidine)

(A) $\left\{Fe(cys)_4\right\}$ (B) $\left\{Fe_2S_2(cys)_4\right\}$

(C) $\left\{Fe_2S_2(cys)_2(his)_2\right\}$ (D) $\left\{Fe_4S_4(cys)_4\right\}$

47. The separation between E_1 and E_3 in the following energy level diagram will be :



(A) 800 nm (B) 400 nm

(C) 200 nm (D) 300 nm

48. The amount of $Na_2SO_4 \cdot 4H_2O$ (MW = 214.14) required to prepare a litre of one molar Na solution is :

(A) 214.14 g (B) 107.07 g

(C) 21.414 g (D) 10.707 g

49. Which of the following molecules contains the highest % of nitrogen by mass ?

(A) HNO_3 (B) $LiNO_3$

(C) $NaNO_3$ (D) KNO_3

50. A 10 mg sample containing $CaCO_3$ and α-Al_2O_3 was analysed by thermogravimetry between 30-800°C. A weight loss of 2.2 mg was observed. The % of α-Al_2O_3 in the mixture is ..... .

(Given : M.W. $CaCO_3$ = 100.0)

(A) 75% (B) 45%

(C) 55% (D) 50%

51. On a 30 cm column, the retention times t_r of A and B are 16.40 and 17.63 minutes respectively. The average number of plates in the column are 3000. The plate height will be :

(A) 1.00 (B) 0.01

(C) 100 (D) 30

52. Twenty ml of an aqueous solution of 0.1 M benzoic acid is mixed with 10 ml ether. After the layers are separated it is determined by titration that 0.5 M benzoic acid remains in the aqueous layer. The distribution ration and % E are :

(A) 3, 50% (B) 4, 60%

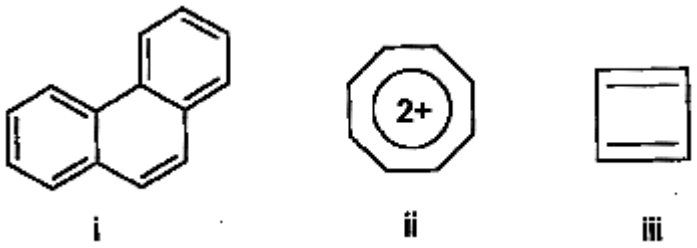
(C) 6, 75% (D) 10, 25%

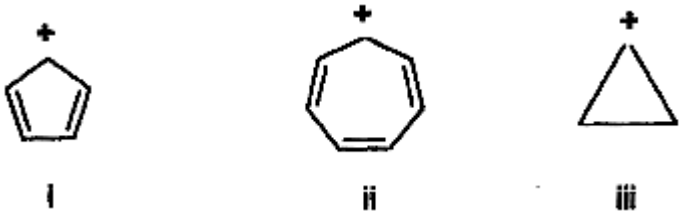
53. Which of the following compounds is *not* aromatic in nature ?

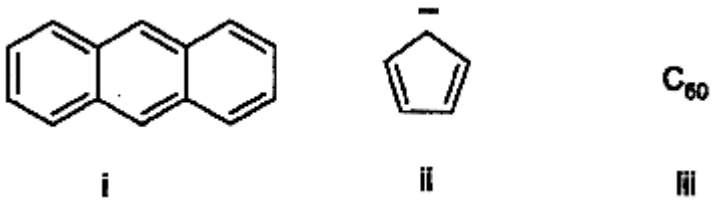
(A) Cyclopentadienyl anion (B) Pyrrole

(C) Fullerene C_{60} (D) Azulene

54. Choose the *correct* option as indicated in series given below :

(*a*) Homoaromatic 

(*b*) Aromatic 

(*c*) Non-aromatic 

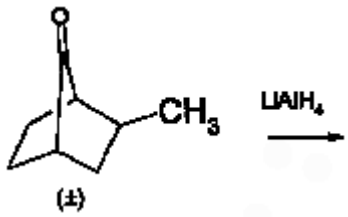
(A) Homoaromatic-i, Aromatic-ii, Non-aromatic-iii

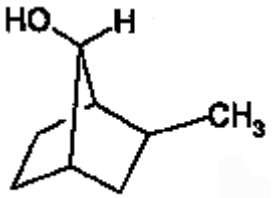
(B) Homoaromatic-ii, Aromatic-iii, Non-aromatic-iii

(C) Homoaromatic-ii, Aromatic-ii, Non-aromatic-ii

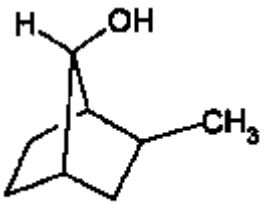
(D) Homoaromatic-ii, Aromatic-ii, Non-aromatic-iii

55. Predict the stereochemical outcome of the following reaction :

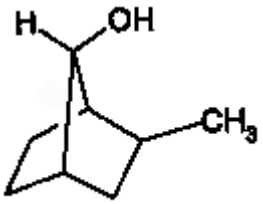


(A) 

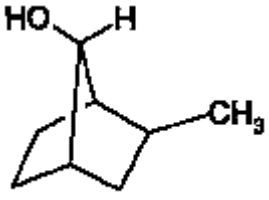
racemic

(B) 

non-racemic

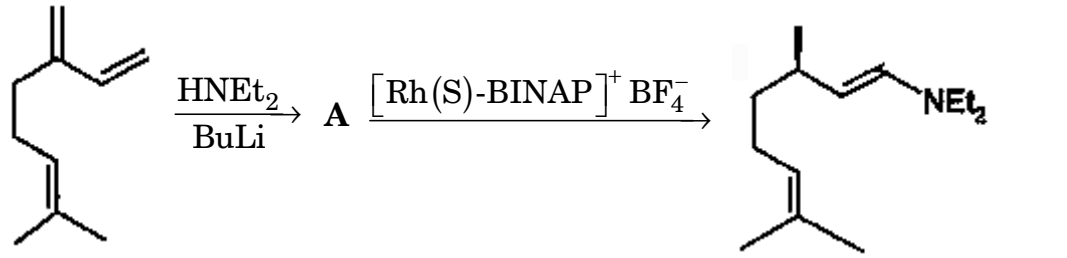
(C) 

racemic

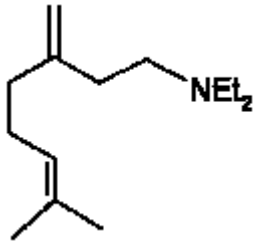
(D) 

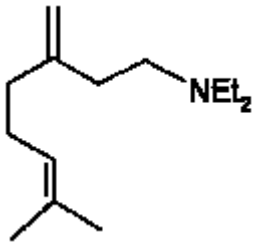
non-racemic

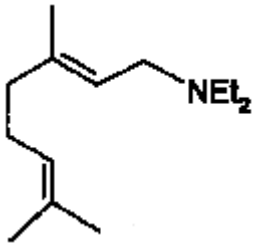
56. Study the following reaction sequence involved in the synthesis of (–)-menthol and choose the *correct* description for the same :

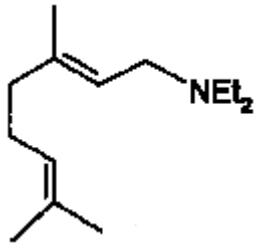


Myrcene Enamine intermediate

(A) Both the steps are non-stereoselective and **A** is 

(B) The second step is enantioselective and **A** is 

(C) The second step is enantioselective and **A** is 

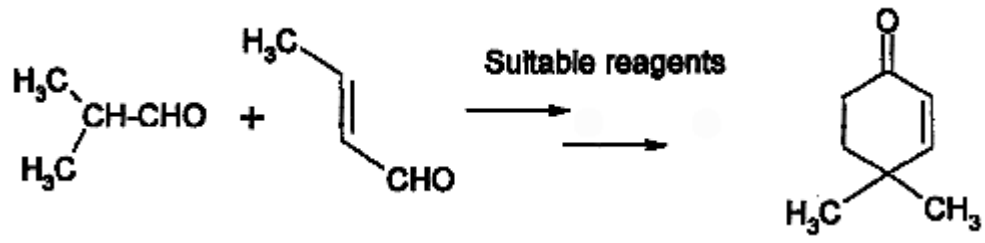
(D) Both the steps are enantioselective and **A** is 

57. In a Shapiro reaction, using 2-octanone, [*p*-tolunesulfonylhydrazone of 2-octanone treated with CH_3Li], the product obtained is :

(A) 1-octene (B) (E)-2-octene

(C) (Z)-2-octene (D) (Z)-3-octene

58. Study the following chemical conversion :



(A) Michael addition followed by cyclization

(B) First aldol reaction followed by Michael addition

(C) Two intramolecular aldol condensations

(D) First Michael addition followed by intramolecular aldol condensation

59. Hammett plots provide useful information about several aspects of a reaction. Match the following aspects regarding reaction constant, ρ and substituent constant, σ, and reactions given.

(L)	Acid catalyzed hydrolysis of ethyl benzoates (ρ = 0.03)	(1)	Reaction proceeds by S_N1 pathway
(M)	Base catalyzed hydrolysis of ethyl benzoates (ρ = 2.51)	(2)	Rate accelerated by *meta*-methoxy substituent and rate retarded by *para*-methoxy substituent
(N)	Solvolysis of benzyl tosylates (ρ = –5.6)	(3)	Indication of two different RDS for EDG and EWG
(O)	Reaction with different signs for ρ for EDG and EWG	(4)	Reaction largely unaffected by polar effects of substituents

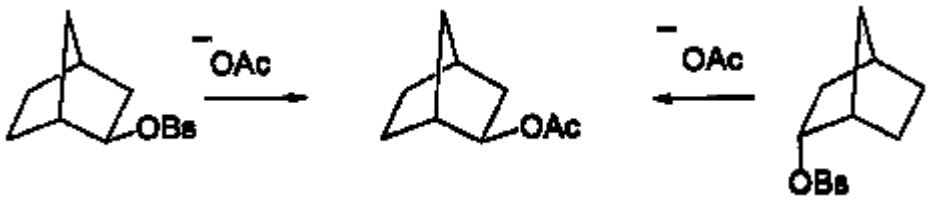
(A) (L)-(1), (M)-(2), (N)-(3), (O)-(4)

(B) (L)-(1), (M)-(4), (N)-(3), (O)-(2)

(C) (L)-(4), (M)-(2), (N)-(1), (O)-(3)

(D) (L)-(2), (M)-(1), (N)-(3), (O)-(4)

60. Study the following reaction :



(I) The *exo* norbornyl brosylate reacts 350 times faster than the *endo* nor bornyl brosylate.

(II) Both *exo* and *endo* brosylates produce exclusively *exo* norbornyl acetate.

(III) Enantiomerically pure *exo* norbornyl brosylate produces 100% racemic product.

(IV) Enantiomerically pure *endo* norbornyl brosylate produces which is slightly non-racemic [%ee < 10%].

Based on these observations, state which of the following statements correctly summarized the above.

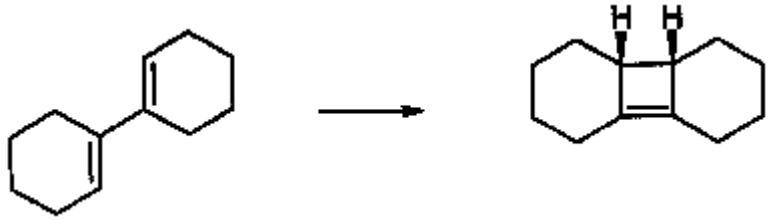
(A) *Exo*-norbornyl brosylate undergoes the reaction with formation of non-classical carbocation and *endo* norbornyl brosylate reacts entirely by S_N2 mechanism.

(B) Both *exo* and *endo* isomers entirely react by formation of classical carbocation.

(C) *Exo*-isomer undergoes reaction entirely by S_N1 and *endo*-isomer undergoes reaction by entirely S_N2 mechanism.

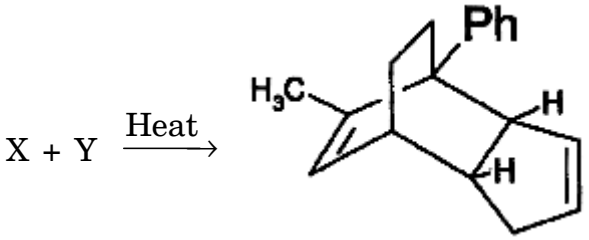
(D) *Exo*-isomer undergoes reaction entirely via formation of non-classical carbocation and *endo*-isomer undergoes reaction partially by S_N2 mechanism and mostly via formation of classical carbocation.

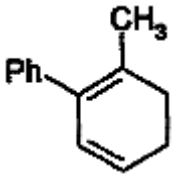
61. Study the following reaction and identify the processes involved :



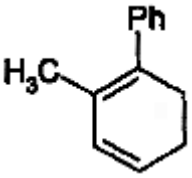
(A) 4 pi electron thermal con-rotatory elecrocyclic reaction.
(B) 4 pi electron photochemical dis-rotatory electrocyclic reaction.
(C) (2 pi + 2 pi) photochemical cycloaddition reaction.
(D) (2 pi + 2 pi) thermal cycloaddition reaction.

62. Identify the structures of missing X and Y components in the following Diels-Alder reaction :

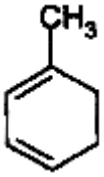


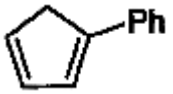
(A) X = 

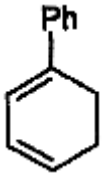
and Y = 

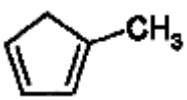
(B) X = 

and Y = 

(C) X = 

and Y = 

(D) X = 

and Y = 

63. The order of increasing reactivity towards nitration is :

(A) Pyridine < quinoline < quinoline-N-oxide

(B) Quinoline < pyridine < quinoline-N-oxide

(C) Quinoline-N-oxide < pyridine < quinoline

(D) Quinoline < quinoline-N-oxide < pyridine

64. Bischler-Napieraski reaction is used for the synthesis of :

(A) Quinoline (B) Isoquinoline

(C) Substituted pyrrole (D) 2-Methyl quinoline

65. In the synthesis of Ph—CO—CH_2—CH_2—CHO using diathiane following reagents are used :

(A) (*i*) NaOMe, (*ii*) CH_2 = CH—CO—Ph, (*iii*) H^+, (*iv*) $HgCl_2/H^+$

(B) (*i*) *n*-BuLi, (*ii*) CH_2 = CH—CO—Ph, (*iii*) H^+, (*iv*) $HgCl_2/H^+$

(C) (*i*) NaOMe, (*ii*) Ph—CH = CH—CHO, (*iii*) H^+, (*iv*) $HgCl_2/H^+$

(D) (*i*) *n*-BuLi, (*ii*) CH_2 = CH—CO—Ph, (*iii*) H^+

66. Prevost and Woodward reactions are useful for formation of 1, 2-diols with opposite stereoselectivities. Which of the following statements is *correct* regarding these reactions ?

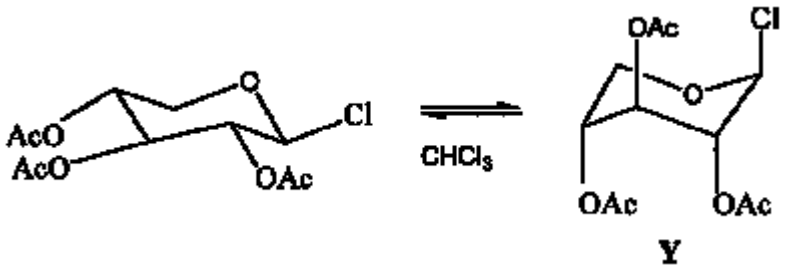
(A) Prevost and Woodward reactions both employ iodine and silver carboxylate. In Prevost dry conditions yield *trans*-1, 2-diol whereas in Woodward reaction *cis*-1, 2-diol is formed in presence of moisture.

(B) Prevost and Woodward reactions both employ iodine and silver carboxylate. In Woodward reaction dry conditions yield *cis*-1, 2-diol whereas in Prevost reaction *trans*-1, 2-diol is formed in presence of moisture.

(C) Prevost and Woodward reactions both employ iodine and silver carboxylate. In Prevost reaction dry conditions yield *cis*-1, 2-diol whereas in Woodward reaction *trans*-1, 2-diol is formed in presence of moisture.

(D) Prevost and Woodward reactions both employ iodine and silver carboxylate. In Prevost reaction *cis*-1, 2-diol in presence of moisture whereas in Woodward reaction dry conditions yield *trans*-1, 2-diol.

67. The major conformer of 2, 3, 4-tri-O-acetyl-β-D-xylopyranosyl chloride in $CHCl_3$ is **Y** with all four groups 'axial'. This is due to the,

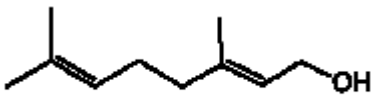


Y

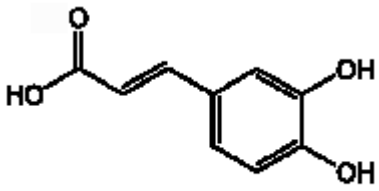
(A) Mutarotation (B) Steric crowding

(C) Hydrogen bonding (D) Anomeric effect

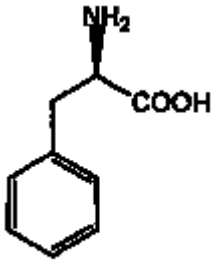
68. Many of the natural product biosyntheses involve shikimic acid pathway. Biosynthesis of one of the following compounds does *not* involve the shikimic acid pathway. Identify the compound :

(A) 

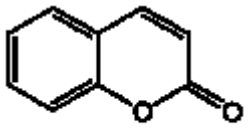
Geraniol

(B) 

Caffeic acid

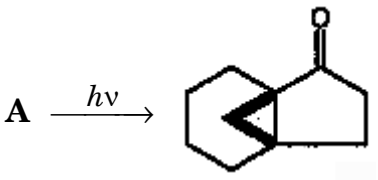
(C) 

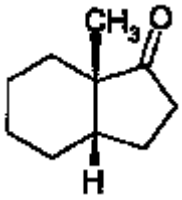
Phenyl alanine

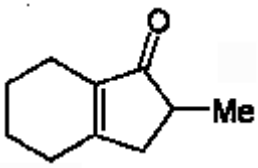
(D) 

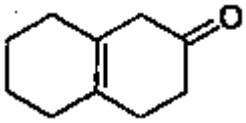
Coumarin

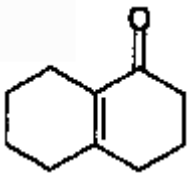
69. The structure of starting material **A** in the following photochemical Norrish type reaction is :



(A) 

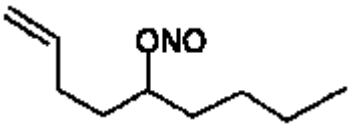
(B) 

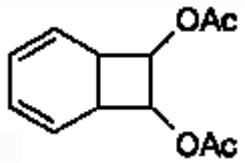
(C) 

(D) 

70. Match the following photo-chemical reactions with their products :

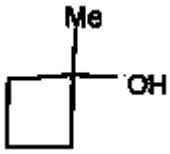
(1) $CH_3CH_2—CO—CHMe_2$

(2) 

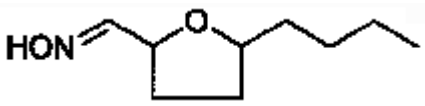
(3) 

(4) $MeCH_2CH_2COMe$

(*a*) 

(*b*) 

(*c*) $(CH_3CH_2CO)^{\bullet}$ and $^{\bullet}(CHMe_2)$

(*d*) 

(A) (1)—(*a*), (2)—(*b*), (3)—(*c*), (4)—(*d*)
(B) (1)—(*c*), (2)—(*d*), (3)—(*a*), (4)—(*b*)
(C) (1)—(*c*), (2)—(*b*), (3)—(*d*), (4)—(*a*)
(D) (1)—(*b*), (2)—(*c*), (3)—(*d*), (4)—(*a*)

71. Protection–deprotection and coupling between two amino acids components are important steps in peptide synthesis. One of the following is *not* used as a protecting group in the peptide synthesis. Identify which :

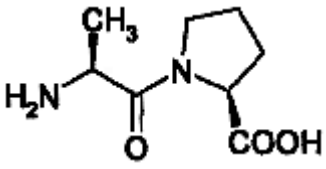
(A) Benzoyloxycarbonyl

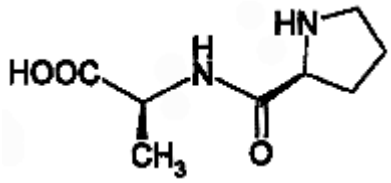
(B) N, N'-dicyclohexylcarbodiimide (DCC)

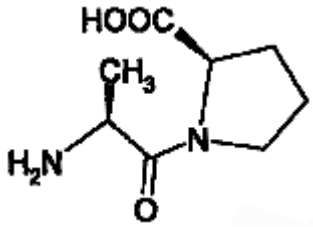
(C) 9-Flourenylmethoxycarbonyl (FMOC)

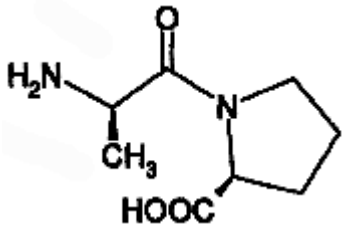
(D) tert-Butoxycarbonyl (BOC)

72. The structure of the dipeptide Ala-Pro derived from the natural amino acids is :

(A) 

(B) 

(C) 

(D) 

73. The proton NMR of 2-bromo-2-methyl propane will show :

(A) Three quartets and a singlet

(B) Two doublets and a singlet

(C) Two singlets

(D) One singlet

74. The ratio of relative intensities of three molecular ion peaks of CH_2Br_2 in the mass spectrum is :

(A) $M^+ : (M + 2)^+ : (M + 4)^+ = 1 : 4 : 1$

(B) $M^+ : (M + 2)^+ : (M + 4)^+ = 1 : 3 : 1$

(C) $M^+ : (M + 2)^+ : (M + 4)^+ = 1 : 2 : 1$

(D) $M^+ : (M + 2)^+ : (M + 4)^+ = 1 : 1 : 1$

75. The number of signals that appear in the PND spectrum of phenanthrene and anthracene respectively are :

(A) Ten and four

(B) Ten and ten

(C) Seven and four

(D) Seven and seven

ROUGH WORK